UTILIZATION OF WASTE

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USE OF MANGANESE-BEARING METALLURGICAL WASTE IN THE PRODUCTION OF INSULATING GLASS

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The possibility of using manganese-bearing waste generated at the Kemerovo Metallurgical Works as a pigment for insulating glass is investigated. It is established that when this waste is treated by magnetic separation and the glass-melting procedure is modified, the waste can be used for steady tinting of glass.

Environmental problems and problems of increasing recycling of industrial waste in the glass industry remain topical. In selecting materials for glass production based on waste generated in other industrial sectors, one takes into account its chemical composition, the presence of undesirable impurities, and the presence of components intensifying the glass-melting process. Constancy of chemical composition of the waste and of the impurity content are the most essential prerequisites. Furthermore, the technological properties of glass and the stability of its tint depend on the redox characteristics of materials used [1].

According to OST 160.800.356–76, various manganese compounds are used at glass factories to impart a violet color to electric-insulating glass. Such colorants, for instance, include pyrolusite, manganese peroxide paste, and potassium permanganate $KMnO_4$. The content of MnO_2 in the best grades of pyrolusite reaches 90%, that of iron oxide not more than 1%, and the quantity of iron compounds occasionally may reach 10%.

In the present study manganese-bearing waste from Kemerovo Metallurgic Works was used to tint insulating glass. The average values of the chemical composition of this waste analyzed during 5 months are represented in Table 1.

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TABLE 1

Oxide	Mass content, %, in sample				
	1	2	3	4	5
SiO_2	17.5	17.3	14.0	16.0	15.0
Mn_2O_3	28.0	28.0	39.0	29.0	29.5
Fe_2O_3	10.0	8.8	4.0	14.0	14.5

It can be seen from the data obtained that the content of colorant oxides in the waste composition varies over a wide range, from 28.0 to 39.0%, and that of iron varies from 4.0 to 14.5%. Due to high fluctuations of the content of colorant oxides in the waste composition, difficulties arose at the Tomsk Electric Lamp Works using this waste, caused by instability of the glass tint: the color of glass varied from light brown to dark violet.

It is known that certain redox equilibriums are formed in a tinted glass melt between variable-valence elements, whose oxides, as a rule, are colorants. The ratios between these oxides depend on the redox state (ROS) of raw materials and glass melt and also on the temperature-gas conditions of melting [2, 3].

In practice, a number of methods are used to control the chemical oxygen minimum (COM) of material, which was determined using the bichromatometry method [4]. The

TABLE 2

Raw material	COM, mg O_2/100 g, in sample			Average value of COM, mg O_2/100 g
	1	2	3	
Sand	45	46	40	43.7
Barite	139	130	136	95.0
Dolomite	70	70	66	68.7
Potash	35	27	32	31.3
Soda	53	58	58	56.3
Coke	632	629	643	634.7
Cullet SL-96-1	99.4	99.06	99.7	99.4
Manganese-bearing waste:				
before treatment	20	65	40	53.0
after heat treatment	42	37	43	40.7
after separation	25	27	26	26.0

TABLE 3

Glass	Mass content, %								
	SiO_2	Al_2O_3	BaO	CaO	MgO	Na_2O	K_2O	Mn_2O_3	Fe_2O_3
SL-96-1	71.90	1.50	2.00	5.50	3.50	16.10	0.98	–	0.10
SL-96-7	62.50	0.75	1.62	5.10	3.05	16.90	0.98	9.10	0.07

TABLE 4

Sample	Chemical composition of glass (found in analysis), wt.%					Glass color	TCLE, 10^{-7} K^{-1}
	Mn_2O_3	BaO	MeO + Me_2O	Fe_2O_3	$SiO_2 + Al_2O_3$		
1	4.1	2.9	25.4	1.1	66.5	Dark violet	99.5
2	4.5	3.4	24.6	1.1	66.4	Light brown	97.5
3	4.7	3.2	24.6	1.0	66.5	The same	97.6
4	4.2	3.2	24.7	1.2	66.7	Dark violet	98.0
5	3.4	3.4	24.8	1.9	66.5	The same	98.3

mean values of COM of materials analyzed at the Tomsk Electric Lamp Works for 3 months are indicated in Table 2.

The most significant spread in COM values (20 – 65 mg O_2/100 g) is observed in the manganese-bearing waste. The instability in the chemical composition of the waste has a negative effect on the tint of the insulating glass; therefore, the waste was subjected to additional treatment for 3 h at a temperature of 500°C and magnetic separation. The COM values of the waste after thermal treatment decreased on the average by 25%, and after magnetic separation, by 50%.

Tinted insulting glass SL-96-7 was melted using recyclable cullet SL-96-1 (Table 3), where 8 wt. parts of manganese-bearing waste and 1.16 wt. parts of soda were added in a recuperative glass-melting tank furnace with a laterally directed flame heated by natural gas. The daily output of the furnace is 3.5 tons, and the glass-melting temperature was 1450°C.

An important property of insulating glass is its TCLE, which determines the possibility of obtaining reliable glass-to-metal seals; therefore, this characteristic was monitored as well. According to OST 160.800.356–76, the TCLE of glass SL-96-7 should amount to $(100 - 2.5) \times 10^{-7}$ K^{-1}. The chemical composition, color, and TCLE of the glasses obtained are indicated in Table 4.

It can be seen that the Mn_2O_3 content and the TCLE values in all samples of the insulating glasses are within the prescribed limits; however, the color of glass in samples 2 and 3 is light brown instead of the violet shade required. At high temperatures Mn_2O_3 is an unstable compound and can be reduced to MnO, which does not tint glass:

$$2Mn_2O_3 \rightarrow 4MnO + O_2.$$

The valence of manganese in the melt depends both on the ROS of the batch and on the melting conditions; therefore the COM of glass and the state of the gaseous atmosphere were monitored by the furnace zones (Table 5).

TABLE 5

Parameter	Zone	Sample				
		1	2	3	4	after treatment of waste and modification of melting conditions
Volume content of O_2 in furnace atmosphere, %	Charging	2.0	1.0	0.6	0.8	–
	Melting	2.8	3.2	2.2	1.0	1.2 – 1.4
Volume content of CO_2 in furnace atmosphere, %	Charging	10.4	11.2	11.2	11.6	11.6
	Melting	9.6	10.0	10.2	11.2	10.4
COM of glass, mg O_2/100 g	Pocket	103.0	101.0	107.0	108.0	106.0
	Melting	63.0	70.0	75.0	71.0	74.0
	Channel	65.0	74.0	78.0	73.0	77.0
	Working	77.0	81.6	86.6	83.0	85.0
Glass color	Pocket			Violet		
	Melting	Light yellow		Brown		
	Channel	Light brown		Brown-violet		Violet
	Working	Brown		The same		The same

It is established that with an oxidizing medium (O_2 content over 2 vol.%) in the melting zone and COM equal on the average to 72 mg $O_2/100$ g in the melting zone and 82 mg $O_2/100$ g in the working zone, the redox processes are shifted toward the formation of reduced forms of manganese. In this case yellow-brown and brown-violet colors are formed in the glass due to the presence of iron in the manganese-bearing waste, which reduces manganese to the bivalent state.

To create the most favorable melting conditions, the waste after heat treatment and magnetic separation was used, the maximum temperature of the gaseous medium was decreased to 1350 – 1400°C, and the oxygen content in the melting zone was brought down to 1.2 – 1.4%. Furthermore, the batch composition was modified: the content of concentrate introduced was increased from 14.85 to 18.34 kg per 100 kg of cullet SL-96-1.

As a consequence of the measures taken, glass of a stable violet color was obtained.

Thus, when correcting the batch composition taking into account the COM of waste materials with an unstable content of colorant oxides and modifying the melting regime, the manganese-bearing metallurgical waste can be recommended for obtaining a steady tint in insulating glass, which is economically effective

REFERENCES

1. A. B. Atkarskaya and V. I. Kiyan, “Mechanism of formation of redox potential in glass,” *Steklo Keram.*, No. 1, 12 – 14 (2002).
2. Yu. A. Guloyan K. S. Katkova, T. I. Balandina, and A. G. Belyaeva, “Redox characteristics of batches and specifics of melting container glasses,” *Steklo Keram.*, No. 11, 4 – 5 (1990).
3. N. A. Pankova, L. A. Orlova, N. G. Lipin, and T. D. Orlova, “Tint of glass ceramic materials depending on redox characteristics of batches,” *Steklo Keram.*, No. 2, 2 – 4 (1994).
4. G. D. Fadeeva, “The effect of redox potential of batch and cullet on color of industrial glass compositions containing iron oxides,” *Steklo Keram.*, No. 10, 3 – 7 (2000).